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Note

Gas chromatographic analysis of thermal degradation products of gingerol compounds in steam-distilled oil from ginger (*Zingiber officinale* Roscoe)

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Steam distillation is the most commonly used process for the extraction of essential oils from aromatic plants such as spices and flowers. It provides a fast and simple way to obtain the aromatic components which bear the characteristic odour of that species. However, "still notes" or "burnt notes" are sometimes found in freshly distilled oil[1,2]. The off-flavour results in most cases from thermally induced hydrolytic or degradative reactions. Ohloff *et al.*[3] reviewed several artifacts induced by steam distillation.

Gingerol compounds, the dominant pungent principles in rhizomes of *Zingiber officinale* Roscoe, are thermally labile due to the presence of a β-hydroxy keto function in their structures[4,5]. In our previous study[6], two homologous series of gingerol compounds, 6-, 8-, 10-, 12-, 14-gingerols and methyl-6-, methyl-8-, methyl-10-, methyl-12-gingerols, were identified in a liquid carbon dioxide extract of ginger. Thermal degradation (retro-aldol and retro-Claisen Schmidt reaction) of the above gingerol compounds during gas chromatographic (GC) analysis produced aldehydes (C_6, C_8, C_{10}, C_{12} and C_{14}) and ketones (2-heptanone, 2-nonanone, 2-undecanone and 2-tridecanone). The presence of hexanal, octanal, decanal, 2-heptanone, 2-nonanone and 2-undecanone in the steam-distilled volatiles of ginger has been reported by several research groups [7–9]. However, it was not known whether these compounds were related to the non-volatile gingerol compounds.

The present study reports the capillary GC analysis of volatile compounds derived from thermal degradation of non-volatile gingerol compounds during steam distillation. Ginger oil extracted by liquid carbon dioxide was used as a control for its extraction at low temperature.

EXPERIMENTAL

Sample preparation

Mature ginger (*Z. officinale* Roscoe) rhizomes were obtained from a supplier near Hsinchu (Taiwan). The rhizomes were washed, sliced, freeze-dried, ground and sieved (200 mesh). Steam-distilled essential oil from ginger powder was obtained by the A.O.A.C. method[10]. Ginger oil was obtained by liquid carbon dioxide extraction as described previously[6]. C_6–C_{14} *n*-Aldehydes were obtained from Polyscience (Niles, IL, U.S.A.). 2-Heptanone, 2-nonanone and 2-undecanone were obtained from Aldrich (Milwaukee, WI, U.S.A.), 2-tridecanone from Caro (Tokyo, Japan). *n*-Alkanes were obtained from Alltech Associates (Deerfield, IL, U.S.A.). Zingerone was obtained from ICN Biomedical (Plainview, NY, U.S.A).

Fractionation of volatile compounds by column chromatography

Steam-distilled ginger oil (0.96 g) and liquid carbon dioxide-extracted ginger oil (1.71 g) were applied separately to a glass column (40 cm × 2.0 cm) packed with silica gel (50 g, 60–200 mesh; Mallinckrodt). The hydrocarbon fraction was eluted with pentane (1 l, Aldrich) and the oxygenated hydrocarbon fraction was eluted with ethyl ether (1 l, E. Merck). The pungent gingerol compounds were not eluted under these conditions. Tetradecane (Matheson, 7.60 mg) and ethyl decanoate (Lachat Chemicals, 3.8 mg) were added the hydrocarbon and oxygenated hydrocarbon fractions, respectively, as internal standards.

GC and GC–mass spectrometric (MS) analysis of volatile components

The oxygenated hydrocarbon fractions from steam-distilled and liquid carbon dioxide-extracted ginger oils were subjected to GC analyses on a Varian 3400 gas chromatograph. Two fused-silica columns, one with a stationary phase equivalent to Carbowax 20M (DB-WAX+, 60 m × 0.32 mm, J&W Scientific), the other with a stationary phase equivalent to OV-1 (SPB-1, 60 m × 0.25 mm; Supelco), were installed. The oven temperature was programmed linearly from 50 to 225°C at 1.5°C/min and was held at 225°C for 50 min. Other operating conditions were as follows: injector and detector temperatures, 250°C; make-up helium flow-rate, 30 ml/min; detector hydrogen flow-rate, 30 ml/min; detector air flow-rate, 300 ml/min. The samples were injected in the split mode with a splitting ratio of 1/100 for the Carbowax 20M column and 1/200 for the OV-1 column. The linear velocity of the helium carrier gas for the Carbowax column was 22 cm/s, and was 21 cm/s for the OV-1 column. Quantitations were performed using a Varian 4270 integrator. Linear retention indices for the volatile components were calculated using C_7–C_{25} *n*-paraffins (Alltech Associates) as references[11].

GC–MS was carried out on an Hewlett Packard 5985 B system equipped with an Hewlett-Packard 5840 A gas chromatograph. Two types of fused-silica columns (Carbowax 20M and OV-1) were used. The analytical conditions were as follows: temperature program, 50 to 200°C, 1.5°C/min, isothermal at 200°C, 50 min; injector temperature, 250°C; helium carrier gas velocity, 30 cm/s; ion-source temperature, 200°C; ionization voltage, 70 eV; electron multiplier voltage, 2600 V.

RESULTS AND DISCUSSION

The adverse effects of steam distillation due to thermal degradation have frequently been discussed[1–3]. In this study, the effect of steam distillation on the formation of volatile aldehydes and ketones from non-volatile gingerol compounds in ginger was investigated. Freeze-dried ginger powder was extracted by two different processes, a high temperature extraction by steam distillation and a low temperature extraction by using liquid carbon dioxide. Using silica gel column chromatography, both ginger extracts were fractionated into hydrocarbon and oxygenated hydrocarbon fractions. Since the hydrocarbon fraction comprises about 71% (w/w) of the total volatile components of ginger[12], removal of this fraction will be helpful for the detection of components in the oxygenated hydrocarbon fraction. GC and GC–MS analyses of both hydrocarbon fractions indicated the presence only of monoterpenes and sesquiterpenes.

Fig. 1 shows the capillary gas chromatograms (Carbowax 20M) of oxygenated hydrocarbon fractions from (A) liquid carbon dioxide extraction and (B) steam distillation. Table I shows the quantitative estimations of aldehydes and ketones from two fractions. Identification of these compounds was accomplished by comparing their retention indices and mass spectra with those of authentic standards using two types of columns, Carbowax 20M and OV-1[13,14]. The quantitative estimation was based on the use of ethyl dodecanoate as an internal standard (peak with a asterisk in Fig. 1).

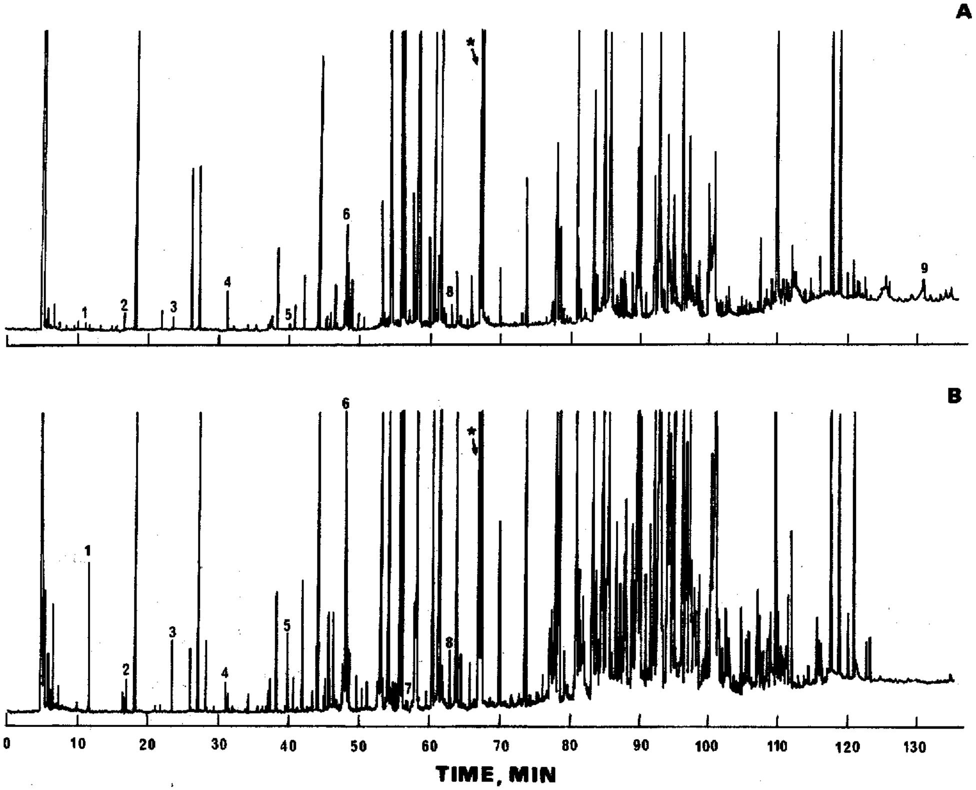

Fig. 1. Capillary gas chromatographic analyses on Carbowax 20M of oxygenated hydrocarbon fractions from (A) liquid carbon dioxide extraction, (B) steam distillation. The peak with an asterisk is due to the internal standard (ethyl dodecanoate).

TABLE I

COMPARISON OF SELECTED OXYGENATED HYDROCARBON COMPOUNDS IN GINGER OIL EXTRACTED BY STEAM DISTILLATION AND LIQUID CARBON DIOXIDE EXTRACTION

*No.**	*Compound*	*Calc. retention index*		*%(w/w)***	
		Carbowax 20M	*OV-1*	*Distillation*	CO_2
1	Hexanal	1072	779	0.045	0.003
2	2-Heptanone	1172	865	0.008	0.010
3	Octanal	1275	979	0.034	0.012
4	2-Nonanone	1380	1062	0.013	0.043
5	Decanal	1483	1185	0.044	0.001
6	2-Undecanone	1586	1274	0.290	0.127
7	Dodecanal	1696	1388	0.005	***
8	2-Tridecanone	1803	1470	0.037	0.020
9	Zingerone	>2500	1596	–	§

* Refers to Fig. 1.

** Average of two determinations, using ethyl dodecanoate as an internal standard.

*** Not present.

§ Trace amount.

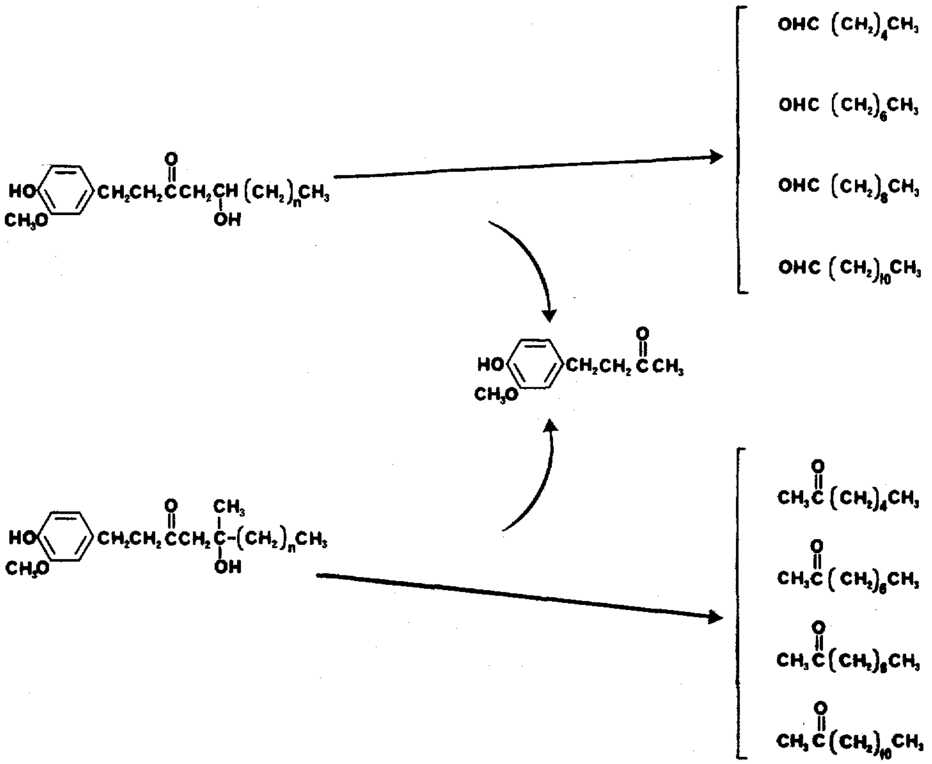

Fig. 2. Scheme of steam distillation-induced degradation of non-volatile gingerol compounds. *n* = 4, 6, 8, 10.

Steam distillation resulted in the retro-aldol (also retro-Claisen Schmidt) degradation of non-volatile gingerol compounds. The significantly higher concentrations of aliphatic aldehydes (C_6, C_8, C_{10}, C_{12}) and 2-alkanones (2-undecanone and 2-tridecanone) in the steam-distilled sample (Table I) confirmed that thermal degradation of gingerol compounds occurred during steam distillation. There was no significant difference between the 2-heptanone found in the two samples. A relatively higher concentration of 2-nonanone was detected in the liquid carbon dioxide extract. Although the concentrations of 2-heptanone and 2-nonanone should be higher in the steam-distilled sample, this may be explained by losses during steam distillation. We were not able to identify the thermal degradation product of 14-gingerol (tetradecanal), a novel gingerol compound previously identified[6], probably because only trace amounts of this compound were present. Attempts to find zingerone, another fragment of retro-aldol degradation of gingerol compounds, in the steam-distilled sample failed, probably due to the less volatile nature of this compound[15]. However, trace amounts of zingerone were positively detected in the sample extracted with liquid carbon dioxide. This is in good agreement with the previous finding of zingerone in the liquid carbon dioxide extract of ginger[16]. The presence of zingerone in a ginger sample can be a good index of the thermal processing of the raw material.

A scheme showing the proposed formation of volatile aldehydes and ketones in ginger due to the degradation of the non-volatile gingerol compounds is shown in Fig. 2.

CONCLUSIONS

The present results indicated the thermal degradation of non-volatile gingerol compounds due to steam distillation. They again confirm the adverse effect of thermal processing upon the flavour quality of ginger. On the other hand, low temperature extraction such as liquid carbon dioxide extraction offers a product devoid of any thermally induced artifacts.

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